USE OF SULFUR ISOTOPES

TO TRACE URANIUM MILL

POND SEEPAGE

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GEOCHEMICAL SULFUR CYCLE

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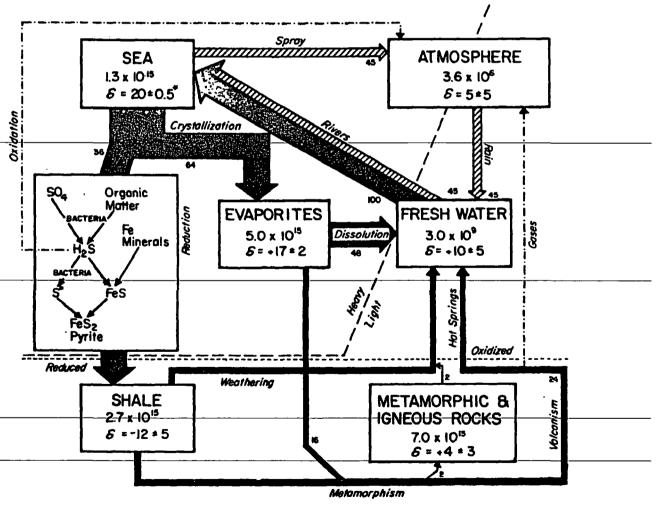
USE OF SULFUR ISOTOPES

TO TRACE URANIUM MILL POND SEEPAGE

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Draft of Final Report

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Introduction

Conclusive evidence for seepage from a uranium mill pond to a local aquifer is often difficult to obtain. Where groundwater contains high concentrations of major and trace ions prior to mining, often the case in areas where uranium mineralization occurs, standard chemical analyses of groundwaters may show sufficient natural variation that contamination may not be obvious. Elevated concentrations of some contaminants are often erroneously ascribed to other causes. Exotic chemical or radioactive solutes introduced to a mill pond are not expected to be effective tracers. Most solutes are unstable, precipitate, or demonstrate sorption under the wide range of chemical conditions encountered as acidic pond waters infiltrate the subsurface. Radioactive tracers can be hazardous and expensive and their use is virtually precluded by regulatory or political considerations. Moreover, the introduction of exotic tracers to these large systems is likely to be impractical. The capacity of a uranium tailings pond is several million gallons; areal extent of the groundwater flow system of interest can be several square miles. Strong motivation exists for selection of an identifiable solute which has been added by the mining or milling process and which is relatively unaffected by subsequent hydrogeochemistry.

This report describes the use of sulfate isotopes as groundwater tracers at the Kerr-McGee section 31 mill site in the Ambrosia Lake uranium mining district, near Grants, New Mexico (Figure 1). Analyses of sulfur isotope composition of dissolved

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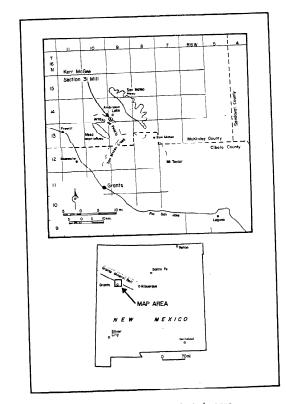
Figure 1. Location map of study area

sulfates from a mill tailings pond, a tailings solution evaporation pond, a mine effluent storage reservoir, a stream, and 22 monitoring wells were used to detect seepage of mill effluent and mine dewatering discharge into an alluvial system. An additional sulfur isotopic analysis was made of the sulfuric acid manufactured at the Kerr-McGee plant.

To our knowledge, this is the first study to use isotopic composition of sulfates to detect mill pond seepage. Therefore, a discussion of the rationale for using sulfate isotopes and a summary of the occurrence and the hydrogeochemical behavior of sulfur isotopes is included in this report.

Rationale for Study

A number of recent investigations have utilized sulfur isotopes to determine the sources of sulfates in natural water systems (Hitchon and Krouse, 1972; Rightmire and others, 1974; Smejkal, 1978; and Fontes and Zuppi, 1976). A logical extension of these studies is the use of sulfur isotopes to identify sources of groundwater contamination from mine wastes, mill pond seepage, and industrial operations.

Sulfate dissolved in precipitation enters groundwater with infiltrating recharge; sulfate also originates within an aquifer from oxidation of sulfide minerals, decomposition and oxidation of organic material, and dissolution of sulfate evaporite minerals. Sulfate is added to groundwater by some industrial processes; sulfuric acid (H_2SO_4) is used as a leaching agent in the uranium, copper, and aluminum industries and is the most commonly used

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industrial acid. All uranium mills in the Grants Mineral Belt except United Nuclear Homestake Partners employ a sulfuric acid leaching circuit (Kunkler, 1979). Isotopic composition can vary considerably between different sulfate sources in a groundwater system. When this is the case, each sulfate carries an isotopic label that can identify its source in a particular sample.

The sulfate anion is potentially doubly useful as a tracer because both sulfur and oxygen atoms can be isotopically analyzed to determine their source and to obtain information on the geochemical history of the sulfate. The Kerr-McGee mill site study will include analysis of the oxygen isotopic composition of sulfate and the stable isotope composition of hydrogen and oxygen in water although only sulfur isotopes are addressed in this report.

Both chemical and isotopic characteristics of sulfates imply their potential as tracers of uranium mill pond seepage. Use of many more commonly used chemical tracers is precluded by drastic chemical changes that occur when solution percolates into the subsurface from mill ponds. Tracers must be stable and retain their chemical characteristics over a pH range from nearly 1 in a tailings pond to 8 in the subsurface.

Sorption, the concentration of solutes onto solid phases, is particularly likely to be affected by pH. Porous media, especially clays which line many tailings ponds, exhibit a negative surface charge that, under normal conditions, repels negative ions. However, under acidic conditions, clay particle edges, metal oxides, and humic materials protonate causing discrete positive surface charges. Under these conditions normally unimpeded anionic tracers may be sorbed.

When leachate penetrates underlying foundation material or geological formations, acid is neutralized, primarily by the following reation with carbonates;

$$H_2SO_4 + CaCO_3 \text{ or } CaMg(CO_3)_2 \rightleftharpoons Ca^{+2} + Mg^{+2} + SO_4^{2-} + H_2CO_3 \quad (1)$$
(sulfuric acid) (calcite or dolomite)

The resultant increase in pH causes many compounds to precipitate and could remove tracers, including sulfate (as anhydrite), before they reach the groundwater system.

However, sulfate is present in extremely high concentrations in uranium tailings ponds (37,400 mg/l in Kerr McGee Pond #1 on 11/9/81). Some sulfate removal by sorption and precipitation occurs, but residual leachate sulfate concentrations are still very high, as shown by SO_4 concentrations in wells adjacent to mill ponds. Neither adsorption nor precipitation should alter the isotopic composition of sulfur in remaining dissolved sulfate (discussed later). Therefore, although sulfate concentration may be reduced during passage through the subsurface, the identity of each sulfate source is maintained.

Characteristics of Sulfur Isotopes

Isotopes are atoms of the same chemical element that have an identical number of protons but a different number of neutrons. Sulfur has 4 stable isotopes whose approximate abundances are: $^{32}S = 95.0\%$, $^{33}S = 0.76\%$, $^{34}S = 4.22\%$, and $^{36}S = 0.014\%$.

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Isotopic composition of sulfur is measured with respect to a standard and expressed as $\delta^{34}S$. $\delta^{34}S$ has units of parts per thousand (termed per mil and denoted as ‰). $\delta^{34}S$ is defined as:

$$\delta^{34}S(‰) = \frac{^{34}S/^{32}S(sample) - ^{34}S/^{32}S(standard)}{^{34}S/^{32}S(standard)} \times 10^3 \qquad (2)$$

The standard is troilite (FeS) of the Canyon Diablo Meteorite, therefore its δ value is 0‰. If the $^{34}S/^{32}S$ ratio of a sample is larger than that of the standard, the sample is enriched in ^{34}S (heavy); its δ value is positive. Similarly, if the $^{34}S/^{32}S$ ratio of a sample is smaller than that of the standard, it is depleted in ^{34}S (light); its δ value is negative.

Fractionation

Almost all variations in the isotopic composition of sulfur are caused by four processes: bacterial reduction and oxidation, isotopic exchange, chemical reduction, and adsorption.

Bacterial reduction is the most important cause of variation in the isotopic composition of sulfur. At a temperature less than 50° C, it is the only mechanism for sulfate reduction. Anaerobic bacteria utilize sulfate to oxidize organic material, producing H_2S that is enriched in ^{32}S. Fractionations of up to nearly 50‰ have been achieved in the laboratory (Hoefs, 1980). On a global basis, sulfate reduction has divided sulfur isotopes into a heavy sulfate fraction and a light reduced sulfur fraction. Typically, reservoirs of hydrogen sulfide (H_2S), elemental sulfur (S), and petroleums produced by bacterial reduction have $\delta^{34}S$ values approximately 15‰ less than the sulfate source (Thode

and Monster, 1965). Recently deposited sulfide minerals in stratified lakes have $\delta^{34}S$ values up to 55‰ lighter than their sulfate source (Deevey and others, 1963; Matrosov and others, 1975). Bacterial oxidation of sulfides may produce sulfates depleted in ^{34}S by up to 14‰ below the sulfide from which they were formed (Nissenbaum and Rafter, 1967).

Figure 2, adapted from Holser and Kaplan (1966), shows the geochemical sulfur cycle and average $\delta^{34}S$ for major sulfur reservoir. Figure 3, from Holser and Kaplan, shows the range in sulfur isotopic composition of each reservoir. Large differences in isotopic composition of each reservoir are noted on a global scale. However, at a given location, each reservoir may have a fairly constant isotopic composition.

Sulfate isotopic exchange reactions involve exchange of sulfur atoms between coexisting sulfur-bearing chemical species. Resulting equilibrium isotopic ratios are governed by equilibrium coefficients. The rates of approach of sulfur to isotopic equilibrium exceed 10^5 years at earth surface temperatures and normal pH (Lloyd, 1968), hence isotopic exchange would not occur rapidly in shallow groundwater systems.

Inorganic chemical reductions that involve breaking the S-O bond in sulfate do not occur at low temperatures and normal pH (Ohmoto and Rye, 1979).

In the absence of sulfate reducing bacteria, the only processes that could fractionate sulfur isotopes in dissolved sulfate as it travels from a mill pond into a groundwater system are precipitation and adsorption on clays. Nriagu (1974)

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Masses of sulfur in metric tons and mean δ are shown for each reservoir (* = Since Late Cretaceous)

— — — Above this line heavy ($\delta > +10‰$) sulfur predominates, and below it light ($\delta < +10‰$) sulfur predominates

------- Material above this line is oxidized, and below it, reduced

Long-term (▶) and short-term (▨) fluxes of sulfur between reservoirs are indicated on the basis of 100 for long-term flux of fresh-water sulfate to the sea
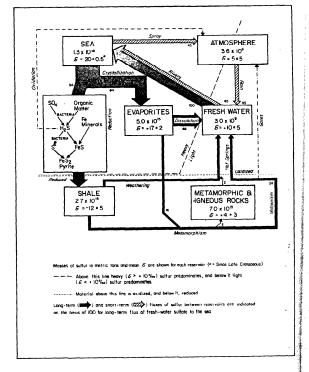
Figure 2. Geochemical sulfur cycle

Figure 3. Range in isotopic composition of major sulfur reservoirs

demonstrated preferential adsorption of ^{32}S-bearing sulfate on an organic rich, low carbonate, clayey sediment. Sodium sulfate (Na_2SO_4) solution of known isotopic composition was equilibrated with washed sediment. After two days the solution was isotopically analyzed. Residual sulfate was found to be an average of 14‰ heavier than adsorbed sulfate. Larger fractionations were associated with lower sulfate concentrations.

In a tailings pond, some sulfate could be adsorbed on slimes that settle to the bottom of the pond thus enriching aqueous sulfate in ^{34}S. However, the high sulfate concentration in tailings solution is associated with smaller fractionations. Sulfate concentrations in the seepage would likely overwhelm the adsorptive capacity of slimes or clays.

Precipitation of sulfate salts removes a large amount of dissolved sulfate during seepage. Thode and Monster (1965) studied fractionation during precipitation of gypsum ($CaSO_4 \cdot 2H_2O$) from a brine solution and found that the precipitated $CaSO_4 \cdot 2H_2O$ was only slightly heavier (+1.65‰) than sulfate in solution. This amount of fractionation should not affect ability to discern sulfate sources with widely different isotopic compositions.

Location of Study Area

The Kerr-McGee Ambrosia Lake mining and milling complex is in the Grants Mineral Belt in the southeastern corner of McKinley County, New Mexico (Figure 1). Kerr-McGee's mill site in Section 31, T.14N.,R.9W. is the focal point of this study. Mines that supply ore to the mill are east, north, and northwest in

sections 17, 19, 22, 24, 30, and 33. Locations of the mill and adjacent ponds are shown in Figure 4; dashed lines delineate the approximate area of subsurface mining.

Kerr-McGee's complex lies in the Ambrosia Lake valley formed by Mesa Montañosa to the south and San Mateo Mesa to the north. The valley is drained by the Arroyo del Puerto which originates northwest of Kerr-McGee's operation (Figure 1). Arroyo del Puerto has been perennial since the 1950's when mine dewatering operations began discharging waters into its course. Arroyo del Puerto joins San Mateo Creek four miles south of the mill site. San Mateo Creek disappears in section 1 or 12, T.13N.,R.10W., indicating recharge to the alluvial aquifer and subsurface flow southeast toward the Rio San Jose (Nylander, 1980; Brod, 1979). Ambrosia Lake, a natural, normally dry, depression contains water only after heavy rains.

Hydrogeology

The following hydrogeologic description of Kerr-McGee's section 31 mill site focuses upon the alluvial aquifer from which samples were collected. Other geologic formations are discussed mainly with respect to their influence on quantity or quality of water in the alluvial aquifer. Much of the information presented in following sections on hydrogeology, flow regime in alluvium, and water balance at the mill site is abstracted from Ganus's (1980) detailed study of the site. Hence references to Ganus (1980) will be omitted where possible in the following sections.

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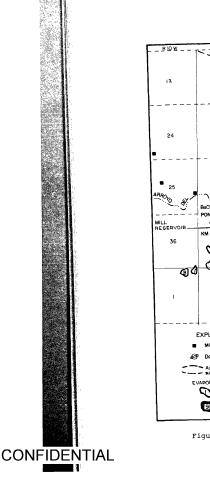
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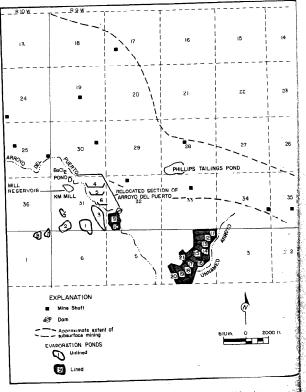
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Figure 4. Map of Kerr-McGee section 31 mill site

Structure

Sedimentary units underlying the study area were flexed by the Zuni Uplift to the south so that the regional dip of these units is now to the north and northeast at 1 to 3 degrees. Post depositional periods of tectonic activity have produced faults and fractures with a predominantly northern trend. Block faulting is recognized in the area; the mill site is on a horst bounded by two faults four miles to the east and west of the mill. Older faults in the area are partially healed and may retard groundwater flow while younger faults increase the rate of groundwater flow. Some shaley layers between aquifers contain significant bentonitic material; where these layers are fractured or faulted they are generally closed and do not permit interaquifer communication.

Figure 5, adapted from Kelly and others (1980), is a geologic map of pre-Quaternary geology of the Ambrosia Lake area. Figure 6 is a cross section, adapted from Brod (1980), taken 0.75 miles southeast of the mill site. The mill site is in the Arroyo del Puerto alluvial valley which rests upon Mancos shale. Younger rock units outcrop as cliffs northeast of the mill on San Mateo Mesa. Older units outcrop south of the site on Mesa Montañosa. A stratigraphic column for the Ambrosia Lake area is also shown to indicate thicknesses of each formation.

Stratigraphy

Uranium ore is mined from the Westwater Canyon Member of the Morrison Formation. Because mining activity does not ordinarily
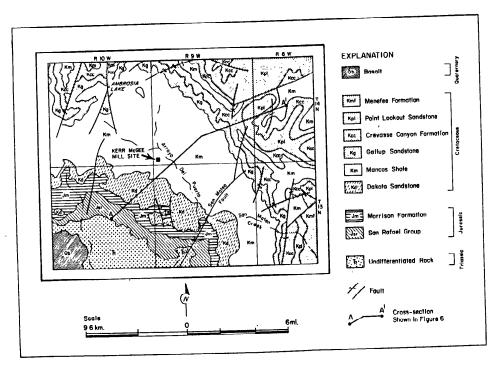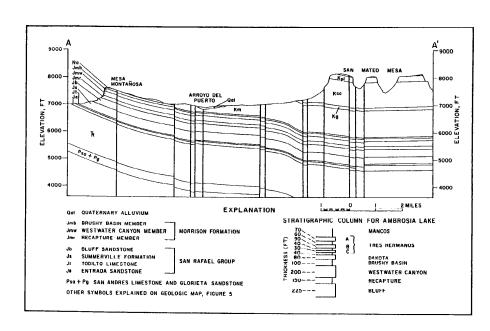
Figure 5. Geologic map of Ambrosia Lake area

Figure 6. Cross-section showing stratigraphy of the Ambrosia Lake area

penetrate a significant distance below this horizon, the following discussion is limited to those units between ground surface and the Morrison Formation. Formations are presented in order from oldest to youngest.

Morrison Formation. The Morrison Formation is composed of three members; the Recapture, Westwater, and Brushy Basin. The Recapture Member is composed of intra-stratified siltstone, shale, and fine sandstone. In the Ambrosia Lake area it is about 100 feet thick and low in permeability, effectively confining the Westwater Canyon aquifer from the underlying Bluff Sandstone.

The Westwater Canyon Member contains the uranium ore body. It is composed of fine-to-coarse grained, poorly sorted arkosic sand and is a significant aquifer. Early data indicate that prior to mining the Westwater potentiometric surface was between 6550 and 6600 feet and that water quality was very good. The Westwater Canyon is approximately 200 feet thick in the subject area.

The Brushy Basin Member consists of 100 feet of bentonitic mudstones and thin sandstone lenses that conform and intertongue with the upper Westwater. This unit acts as a good aquitard overlying the Westwater Canyon aquifer. Uncased wells left open in the unit quickly seal due to the expansive nature of the clay.

Dakota Sandstone. The Dakota is a fine-grained, clean sandstone with fair to good permeability. Historical data indicate that its pre-mining potentiometric surface was close to or slightly above that of the Westwater Canyon aquifer; approxi-
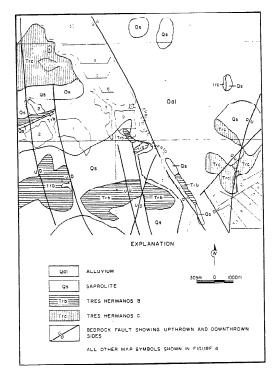
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mately 6000 feet. The Dakota is about 80 feet thick in the study area; water quality is variable.
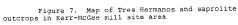
Mancos and Tres Hermanos. Overlying the Dakota Sandstone is the Mancos Shale which contains several sandstone lenses identified as the Tres Hermanos sands. The sandstone lenses are referred to as a, b, and c, from lowest to highest. Tres Hermanos sandstones cap most low hills around the mill site. Much of the rock has become deeply weathered and is mapped as saprolite. Due to weathering, the Tres Hermanos is often difficult to distinguish from overlying alluvium. Figure 7 shows outcrops of the Tres Hermanos and saprolite in the mill site area (Santos and Thaden, 1966). It has been reported that very few data are available describing the Tres Hermanos prior to mining and that these sandstones yield very little water unless fractured. However, east of the area high yields from the sandstones are reported. Cooper and John (1967) reported that the "middle sandstone bed of the Mancos" yielded 900 and 200 gpm to two mines in the San Mateo Mesa area and Brod (1980) reported that the Tres Hermanos is very productive at the Mt. Taylor Mine. Well #31-01 completed in Tres Hermanos-b was artesian when drilled in 1977.

Alluvium. Erosion of Mancos and Tres Hermanos units produced a narrow, 100 foot deep canyon between San Mateo Mesa and Mesa Montañosa. The canyon was subsequently filled by fluvial and eolian deposits 90 to 100 feet thick. Figure 8, from Ganus (1980), is an isopach map of the alluvial deposit. Well logs show that the alluvial material is fine-grained sand and clay with occasional basal gravel layers. Layering or stratification

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Figure 7. Map of Tres Hermanos and saprolite outcrops in Kerr-McGee mill site area

EXPLANATION

Qal	ALLUVIUM
Qs	SAPROLITE
Trb	TRES HERMANOS B
Trc	TRES HERMANOS C

BEDROCK FAULT SHOWING UPTHROWN AND DOWNTHROWN SIDES

ALL OTHER MAP SYMBOLS SHOWN IN FIGURE 4

305m   0   1000ft

Figure 8. Isopach map of alluvium

EXPLANATION

ALLUVIUM BEDROCK CONTACT

—70— LINE OF EQUAL THICKNESS OF ALLUVIUM (FT)

305m   0   1000ft
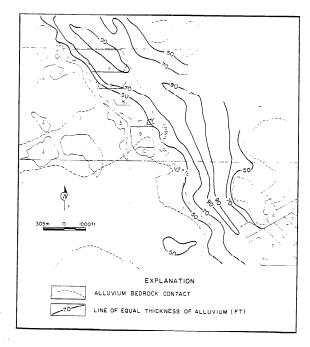
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is often reported.

Kerr-McGee monitoring well #25 was developed in alluvial material three years after mining and milling began. At this site, a small saturated zone at the base of the alluvium was attributed to early mining activity. The well, in section 31, T.14N.,R.9W., was destroyed in 1976 when Arroyo del Puerto was rerouted. Depth to water at that time was 76 feet indicating that 10 feet of alluvium were saturated. Parts of the alluvium in contact with Tres Hermanos sandstone probably contained some water prior to mining.

Hydrologic Effects of Mining and Milling

By 1957 shaft construction and aquifer testing in the West-water Canyon had begun; much of this early discharge was directed into Arroyo del Puerto or its tributaries causing perennial flow in the arroyo that reached San Mateo Creek several miles to the south. Discharge also created a line source of recharge to the alluvium. This discharge was originally good quality water pri-marily from the Westwater. As described in the following section, quality of mine water discharge has constantly decreased since mining began. Where shafts encountered significant amounts of water in the Dakota or Tres Hermanos, these waters were also pumped to the Arroyo del Puerto. Ventilation shafts were drilled throughout the mined area indicated in Figure 4. Water-bearing zones from ground surface to mine level were permitted to drain into the ventilation holes. A local groundwater depression, or sink, has therefore been created in all aquifers from the Westwater Canyon upward.

The section 31 mill began operations in October, 1958. The mill reservoir, tailings pile and pond (pond #1), decant pond for pond #1 (pond #3), and evaporation ponds #4, #5, and #6 were constructed (Figure 4) on local, clay-poor materials. Large seepage losses have therefore occurred from all ponds.

Excess mine water from the mill reservoir has always been pumped to Arroyo del Puerto. In early 1960, mine water infil-trating alluvium through the Arroyo del Puerto and mill reservoir contained 200 mg/l sulfate, 20 mg/l chloride, 600 mg/l total dissolved solids (TDS), and had a pH of 7. Tailings pond solutions seeping into the alluvium contained 26,000 mg/l sulfate, 2,000 mg/l chloride, 40,000 mg/l TDS, and had a pH of 1-2.

Ponds #7 and #8 were constructed in early 1961. From early 1960 until early 1975, ponds #4, #5, and #6 were not in use. Ponds #9 and #10 were constructed in 1976; these were the first plastic lined ponds at the site. In late 1976 and early 1977, plastic-lined ponds #11 through #15 were constructed; lined ponds #16 through #21 were completed in early 1980.

In 1976 the course of Arroyo del Puerto was realigned near the mill site to divert potential flood flows around ponds and tailings (Figure 4).

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This complex water discharge history complicates interpretation of evolution of water quality recharge to the alluvial aquifer. Furthermore, chemical composition of infiltrating water from Arroyo del Puerto differs from that in the tailings pond. Significant quality differences between tailings and evaporation pond water are also evident. The following description of Kerr-McGee's milling process addresses chemical evolution of tailing and evaporation pond water.

Milling Process

Kerr-McGee's acid leach uranium milling process is shown in schematic in Figure 9. Water is pumped from mines into a series of settling ponds. $BaCl_2$ is added to precipitate $BaSO_4$ and co-precipitate $RaSO_4$. Mine discharge waters are then pumped to the mill reservoir. The decreasing quality of mill reservoir water with time, shown in Table 1, probably reflects use of mining practices such as water recirculation to leach uranium from mined areas and backfill operations that emplace mill tailings in mined out areas to prevent roof collapse. Both practices degrade the quality of water pumped from mines and discharged to the mill reservoir and Arroyo del Puerto.

The uranium leaching and concentration process requires addition of various chemicals. Mill reservoir water is mixed with crushed ore in stage 1, size reduction. Sulfuric acid (H_2SO_4) is added to dissolve uranium minerals, forming complex uranyl ions such as $UO_2(SO_4)_2^{2-}$ and $UO_2(SO_4)_3^{4-}$ that are stable only at high H_2SO_4 concentrations. At this low pH (0.5 in the

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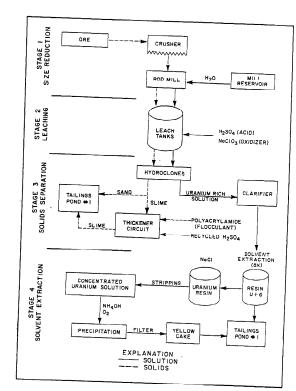Figure 9. Schematic of Kerr-McGee uranium leach circuit

Table 1: Concentrations of sulfate (SO_4), chloride (Cl), and total dissolved solids (TDS) in Kerr-McGee mill reservoir (1958-1981)

(mg/l)	1958 start of mill operation	1980 yearly average	11/9/81 study sampling trip
Cl^-	20	82	58
SO_4^{2-}	200	1084	1188
TDS	600	1928	2056
pH	7.0	7.9	8.1

mill circuit) gangue minerals of vanadium, selenium, molybdenum, and other metals are also dissolved. Sodium chlorate ($NaClO_3$) is added in the leach circuit to oxidize iron minerals such as pyrite (FeS) to produce the ferric ion (Fe^{+3}) which in turn oxidizes uranium from a (+4) to a (+6) oxidation state soluble form.

Solid tailings are separated in stage 3 of the milling process. Hydroclones centrifuge the finer slimes from sands; the uranium rich solution is decanted to a clarifier. Both sands and slimes are washed with recycled sulfuric acid before disposal to pond #1. Slimes enter a 6-stage thickener circuit where an organic flocculant, polyacrylamide, is added. Suspended solids settle beneath a uranium rich solution portion. Both the barren sands and separated slimes are disposed into pond #1.

Uranium is removed from the decant solution by solvent extraction in stage 4. An organic solvent, dodecanol and tertiary amine exchanger, selectively removes uranium ions from solution; organic and acid phases are separated, the acid is recycled to stage 3 or sent to the tailings pond. Chloride, as NaCl, is added in the solvent extraction cycle to strip uranium ions from the organic solvent by anion replacement. The uranium-stripped, chloride rich, aqueous phase is then pumped to the tailings pond (pond #1).

Excess pond #1 fluids are decanted to pond #3. Table 2 compares chemical composition of tailings pond solution with that in the decant pond. Three factors may contribute to the

Table 2: Chemical composition of solution in ponds #1 and #3

(mg/1)	Tailings solution in pond #1			Decant solution in pond #3
	11/16/78*	11/6/79*	11/9/81	11/9/81
TSS	-	98	-	-
TDS	29,523	40,002	44,484	10,844
cond (μmho)	-	45,320	-	-
pH	-	1.33	-	-
As	5.586	2.870	-	-
Ba	0.150	0.231	-	-
Se	0.700	2.788	-	-
Mo	1.429	21.822	-	-
NH_3	396.000	368.000	-	-
Na	1,759.500	1,895.000	1,327	800.4
Cl	2,250.200	2,199.600	2,774	989.8
SO_4	24,476.000	29,819.000	37,483	6,454.0
Ca	432.000	224.000	756	410.9
K	82.680	97.900	109	24.6
Mg	-	1,777.000	1,195	502.9
Cd	0.0263	0.018	-	-
NO_3/NO_2	9.0300	15.640	-	-
V	85.5000	106.750	-	-
Zn	7.0500	6.910	-	-
Al		1,250.000	-	-
Pb	0.996	1.615	-	-
U	16.200	13.400	-	-

* from EID, 1980

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dramatic decrease in concentration of all constituents in pond #3. Most important of these is undoubtedly dilution; pond #3 receives lower salinity water from the dam on Arroyo del Puerto. High total dissolved solids input to pond #1 may establish a density gradient causing stratification. Water is decanted from the surface of pond #1, hence the lightest, least saline water is removed. Precipitation of some compounds and adsorption on clays probably reduces solute concentration by a small amount.

A pumping station at the northern end of decant pond #3 periodically pumps fluid to evaporation ponds.

Response of Hydrologic System to Mining and Milling

Prior to mining, all aquifers in the Ambrosia Lake area were essentially saturated to their outcrops. Mining has created a groundwater depression south of the mined area shown in Figure 4. The Westwater Canyon Member is largely dry due to pumping and the Dakota has been significantly drained by ventilation shafts. Some tailings solution is believed to have entered the Dakota where pond #8 is built upon it.

Tres Hermanos

Analysis of response of the Tres Hermanos is complicated by difficulty in identifying or distinguishing each sandstone layers. Furthermore, most of the alluvial valley rests on these sandstones. Where monitoring wells were emplaced, basal alluvium and Tres Hermanos were screened in the same well.

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Some tailings solution may have entered the middle member of the formation, probably along faults and fractures, originating where Tres Hermanos-b is in contact with pond #2.
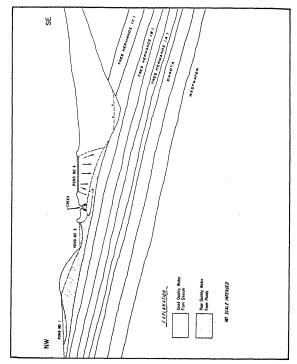
Alluvium

The greatest impact of mining and milling has been on the alluvium. The alluvium was considered nearly dry prior to mining, but now is nearly full of water of mixed composition originating from Arroyo del Puerto and the mill ponds.

Aquifer tests and mine discharge to Arroyo del Puerto started as early as 1957 and began to recharge the alluvial aquifer. By 1958 the mill reservoir (located on weathered Tres Hermanos) and ponds #1 through #6 (located on alluvium) were in use and contributing recharge to the alluvium through seepage. Figure 10, a cross section from pond #1 in the southwest to the northeast across the alluvial valley taken from Ganus (1980), depicts late 1950's conditions. Infiltration of high quality mine discharge water occurred along Arroyo del Puerto, mixed with high TDS and acidic water from the ponds, and flowed toward the deepest part of the alluvium.

Wells #25 and #41 were the first drilled in alluvium at the site. Both show increasing chloride levels with water-level rise. Rate of increase in chloride concentration indicates a dilution or dispersion front expected from mixing of tailings solution with high quality water in Arroyo del Puerto.

Figure 11 is a water level map constructed from measurements

Figure 10. Northwest-southeast cross-section showing conditions in alluvium for the 1959-1960 period

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EXPLANATION
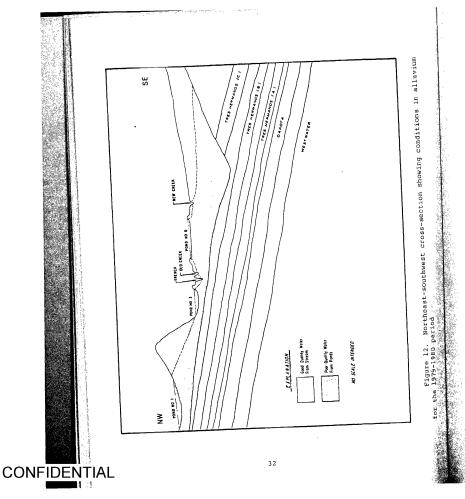
~~~~~ ALLUVIUM/BEDROCK CONTACT

●5-02 Al-Trb WELL NUMBER AND FORMATION IF OTHER THAN ALLUVIUM

6878 WATER TABLE ELEVATION (FT MSL) MEASURED 1/82
SECTION 4 WELLS MEASURED 6/81

----- GROUNDWATER FLOW PATH

6980 CONTOUR SHOWING WATER TABLE (FT)

ALL OTHER MAP SYMBOLS SHOWN IN FIGURE 4
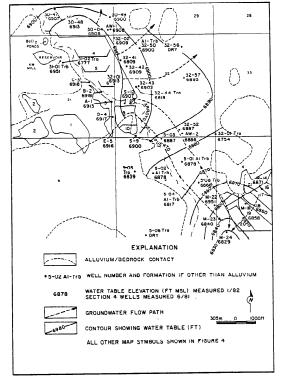
305m   0   1000ft

Figure 11. Water table map for alluvium (1982)

taken in January, 1982 (provided by Kerr-McGee). Contours are drawn from data on wells completed only in alluvium or in alluvium and the b-horizon of the Tres Hermanos Sandstone. Water level data show clearly that, at least east of Arroyo del Puerto, the Tres Hermanos-b is in hydraulic contact with alluvium. The Tres Hermanos-a is confined or semi-confined by interlayered Mancos Shale. Wells 5-05, 33-02 and 32-44, completed in Tres Hermanos-a (Figure 11), have head values up to 100 feet less than those measured nearby in the Tres Hermanos-b. Well 31-02, completed in Tres Hermanos-a, has more than 200 feet less head than that in well 31-01, completed in Tres Hermanos-b.

Figure 11 shows that groundwater exits the alluvial basin to the north, east, and south. Groundwater flow from under ponds #11 through #21 (Figure 4) toward Arroyo del Puerto is also indicated. Ponds #11 through #21 lie in a small arroyo that possibly receives discharge from the Kerr-McGee section 35 mine.

Figure 11 also shows that along most of Arroyo del Puerto's natural course the water table is at the stream bottom. The water table is still below stream bottom on the realigned section of Arroyo del Puerto, but infiltration will eventually cause the water table to rise to the stream bottom.

As a comparison to Figure 10, Figure 12, taken from Ganus (1980), shows present day flow conditions in the alluvium. The new creek has been added; the water table is at the creek bottom. A trench to intercept seepage was excavated in 1959 east of pond #3 and deepened in 1972. Fluid intercepted by the trench is returned to pond #3.

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Figure 12. Northeast-southwest cross-section showing conditions in alluvium for the 1979-1980 period.

Comparison of Figure 11 with a water table map prepared by Ganus (1980) from water levels measured in 1980 and with a less detailed map from Brod (1980) shows that since 1980 the water table has declined slightly near ponds #4, #5, and #6 and risen slightly north and east of these ponds and the realigned stream. This phenomenon reflects decreased use of ponds #4, #5, and #6 and possibly decreased infiltration along the realigned section of Arroyo del Puerto. Outflow of the groundwater mound created beneath these ponds has occurred. The 1982 water level contours are essentially the same as those of Ganus (1980) in the narrow southern part of the Arroyo del Puerto valley.

Flow in alluvium. A large groundwater mound in alluvium formed by seepage from ponds and the Arroyo del Puerto is moving fluid to the north, east, and southeast. To the north, groundwater is reported to be largely intercepted by ventilation shafts and faults and fractures in bedrock. Fluid movement to the east appears to be slow. The water table gradient east is gentle due to the Arroyo del Puerto Creek bottom acting as a limiting factor in preventing additional buildup in mound height. Water flows southeast into the San Mateo alluvial basin to the south.

Groundwater flow velocity in the saturated zone is a function of water table gradient, hydraulic conductivity, and effective porosity. Aquifer tests performed in 1980 at wells AW-1 and AW-2 were analyzed by Ganus (1980); average hydraulic conductivity of alluvium was determined to be 10 gpd/ft^2 (1.3 ft/day). Using the water table gradient shown in Figure 11 and an effective

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porosity assumed to be 20%, approximate flow velocities are 35 ft/yr. to the north, 12 ft/yr. to the east, and 22 ft/yr. to the south. From 1980 water levels, Ganus (1980) calculated similar velocities of 38 ft/yr. to the north, 14 ft/yr. to the east, and 18 ft/yr. to the southeast.

Volumetric flowrates have been determined from the saturated thickness of alluvium and calculated groundwater velocities. Estimates based on 1980 water levels (Ganus, 1980) and on 1982 water levels are similar and indicate 25-30 gpm of flow to the north, 15-20 gpm to the east, and approximately 10 gpm to the south. Flow to the south does not include underflow from beneath ponds #11 through #21 which is estimated to have a velocity of 26 ft/yr.

The alluvial aquifer is now approaching steady state conditions, shown by the similarity of 1980 and 1982 water levels and that near the mill site, and the alluvium is nearly saturated to the surface. Changes in water use and disposal practices cause some fluctuation in the flow system.

Water Balance

A water budget prepared from 1979 data by Ganus (1980) is described below to indicate present quantities of recharge to the alluvium from ponds and the Arroyo del Puerto. Unfortunately, neither water produced, nor discharge scenarios have been constant historically. Records of past practices do not exist. Therefore, the following water budget is probably not representative of past conditions which remain unknown. Quality of

millpond and mine waters were discussed in previous sections. Figure 13 is a schematic diagram taken from Ganus (1980) showing the 1979 water balance for the Kerr-McGee mill.
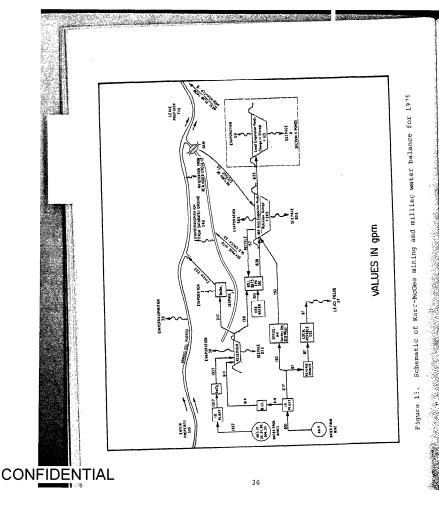
Mine water

Mine water flows to lined and unlined settling ponds before being pumped to the mill. Unlined ponds have a constant seepage loss that is small compared to mine discharge. During 1979 an average of 2,209 gpm reached the mill from mines. Historical discharge is unknown but, based on total pumpage, it was estimated that an average 3,000 gpm have been pumped from mines over the 19 year history of Kerr-McGee's mining operation at Ambrosia Lake.

Mill water

After passing through the ion exchange plant (IX), 230 gpm of mine water are used for drinking and sanitation at the mill and mine office. This water is ultimately disposed of into pond #3. Remaining mine water is sent to the mill reservoir. In 1979 an estimated 30 gpm were lost from the reservoir by evaporation and 273 gpm were lost by seepage; 1381 gpm were used for milling and discharged with slurry to tailings pond #1. Discharge to the tailings ponds also included 100 gpm of ore moisture and 157 gpm derived from recycling tailings water within the mill. Total 1979 discharge to the pond averaged 1638 gpm. Water in excess of milling needs, 283 gpm, was treated with barium chloride, then released to Arroyo del Puerto.

Figure 11. Schematic of Kerr-McGee mining and milling water balance for 1979.

VALUES IN gpm

Arroyo del Puerto

Arroyo del Puerto is dry north of United-Nuclear Homestake IX Plant in section 25, northwest of the mill (Figure 4). United-Nuclear contributes substantial discharge to Arroyo del Puerto; an average of 510 gpm reached Kerr-McGee's property in 1979. Kerr-McGee discharged 283 gpm to the creek from the mill reservoir in 1979.

As previously mentioned, Arroyo del Puerto was rerouted around ponds #1 through #6 in 1976. The new creek rejoins the original creek bed near the northeast corner of pond #9. Drainage from the abandoned creek (about 35 gpm) is contained behind a small dam (Figure 4) and pumped back to pond #3. Flow in Arroyo del Puerto continues four miles downstream to its confluence with San Mateo Creek. Due to changes in mining practices, quality of discharge to the creek has declined similar to that of mill reservoir water shown in Table 1.

Based on water quality changes along Arroyo del Puerto, Ganus (1980) calculated that 8 gpm enter the creek from groundwater baseflow.

Evaporation Ponds

Table 3, from Ganus (1980), shows physical characteristics of ponds #1 through #10. Plastic lined ponds #11 through #21 cover an area of approximately 0.5 square miles; their volumes were not reported.

Fluid in pond #2, #7, and #8, west of the tailings pond #1, is in direct contact with the Tres Hermanos and/or Dakota.

Table 3: Physical characteristics of Kerr-McGee ponds
          #1 through #10 (1979)

Pond #	Area (Acres)*	Volume (Acre-feet)*	Date of Construction	Remarks
1	62	372	1958	Unlined
2	46	299	1958	Unlined; in contact with Tres Hermanos (outcrop)
3	27	53	1958	Unlined
4	13	26	1958	Unlined
5	11	16	1958	Unlined
6	8	16	1958	Unlined
7	12	13	1961	Unlined; in contact with Tres Hermanos (outcrop)
8	24	24	1961	Unlined; in contact with Dakota (outcrop)
9	24	73	1976	Plastic lined
10	7	17	1976	Plastic lined; needs remedial work

TOTALS (Approximately)

234	909
Acres	Acre-feet

* Maximum reported in 1979

Leakage from these ponds via fractures is believed to cause contamination of wells to the north. Seepage from unlined ponds in 1979 was calculated at 203 gpm or 1 gpm per acre of pond. Lined ponds #11 through #20 (section 4 ponds) were reported not to seep.

In unlined ponds, approximately two-thirds of the solution was lost by evaporation while one-third was lost as seepage during 1979. However, the ratio of evaporation to seepage loss decreases with pond depth. Therefore, past seepage rates were probably not comparable to present rates if ponds were less full.

Results of Sulfur Isotope Study

Preceding sections of this report presented background isotopic information and hydrogeologic setting of the Kerr-McGee mill site. The following sections include results and interpretation of chemical and isotopic data developed in this study.

Sample collection. Twenty-eight samples of well, mill pond, and Arroyo del Puerto waters and one sample of mill circuit sulfuric acid were collected for sulfur, oxygen, and hydrogen isotope and chemical analysis on November 9 and 10, 1981 at the Kerr-McGee Ambrosia Lake mill site. Sampling locations and $\delta^{34}S$ values of each sample are shown in Figure 14.

Wells were sampled by bailer; pond and river samples were obtained as "grab" samples. At each sampling location two one-liter polyethylene containers were filled with water for sulfate isotope analysis. About 10 mls of formaldehyde were

EXPLANATION

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-27.9 $\delta^{34}S$ OF SAMPLE (‰)

•5-04   MONITORING WELL OR POND NUMBERS

SAMPLING DATE   11 9 81

ALL OTHER MAP SYMBOLS SHOWN IN FIGURE 4

Figure 14.   Sampling location map showing $\delta^{34}S$ value of samples

added to these samples to prevent bacterial sulfate reduction. Temperature, pH, conductivity, well depth and depth to water were measured in the field at each well location. A Hach Kit test for hydrogen sulfide (H_2S) was performed on each well sample to detect possible bacterial sulfate reduction. Water samples were collected by representatives of the New Mexico EID for major ion, trace metal, and stable oxygen and hydrogen iso-topic analysis. Samples were filtered through a Millipore 0.45 micron cellulose acetate membrane filter. Samples for major ion analysis were placed in one-liter polyethylene bottles; samples for trace metal analysis were acidified with sulfuric acid and sealed in one-liter polyethylene containers. Oxygen and hydrogen isotopic analysis samples were collected by filling one-liter glass bottles to the top; bottles were sealed with paraffin.

Analytical Methods

At the time of this report, results of trace metal and hydrogen and oxygen isotope analysis are not yet available, hence those analytical procedures will not be discussed. Major ion analyses were performed using standard methods by the New Mexico Laboratory in Albuquerque. Sulfur isotope analysis is detailed below; results of all available analyses are presented in Table 4.

Sulfur isotope ratios. Samples were first filtered through a 0.45μ Millipore apparatus to remove any suspended solids before separation of sulfate. To assure a pure $BaSO_4$ precipitate and "clean" conversion to sulfur dioxide gas in the vacuum line,

Table 4. Chemical and sulfur isotope characteristics of waters from Kerr-McGee mill site

* New Mexico State Laboratory, Albuquerque   ** University of Arizona Isotope Geochemistry Laboratory, Tucson   N = negligible

Sample location or well #	Field Measurements				Water elevation (ft. MSL)	Major ions (mg/l)*							TDS	$\delta^{34}S$** (‰)
	T (°C)	pH	Specific conductivity (umhos)	H_2S (mg/l)		Na^+	Ca^{+2}	Mg^{+2}	K^+	HCO_3^-	SO_4^{-2}	Cl^-		
1X Discharge	16	8.1	2,050	-	-	392.1	226.5	70.0	9.75	394.7	1,188	58.3	2,056	-11.0
Pond #1	14.5	1.4	36,000	-	-	1,127.6	755.7	1,194.8	139.2	<1	37,483	2,774.4	44,484	+3.7
Pond #3	-	-	-	N	-	300.4	509.2	410.9	24.6	204.1	6,454	589.8	10,844	-1.1
Cattails P-12 discharge mill	-	-	-	N	-	366.8	206.0	45.8	16.4	204.1	1,034	249.1	1,956	-8.4
Arroyo del Puerto (P-10)	-	1.4	>50,000	N	-	1,116.0	995.0	1,991.2	112.5	<1	38,337	2,608.1	41,960	-
A1	17.5	6.38	-	N	6,911.66	174.2	206.4	78.7	16.4	196.1	1,008	237.1	1,948	+4.5
B2	17.4	5.5	-	N	6,913.90	1,190.0	384.3	439.1	21.1	<1	7,913	2,569.3	16,404	+10.4
C3	18.4	5.07	-	N	6,913.25	1,022.6	346.7	439.1	3.5	<1	3,669	4,038.2	10,564	+0.2
D4	17.6	5.5	-	N	6,912.32	1,115.0	485.2	947.3	9.75	<1	4,557	3,479.9	11,556	-13.6
E5	7.8	8.4	-	N	6,914.24	1,560	1056.0	343.4	10.14	<1	867	2,836.8	6,200	+3.9
S9	14.0	8.4	10,000	N	6,899.87	1,560	159.2	881.5	12.6	3,053	3,053	2,860.8	8,332	-1.9
S12	17.6	6.77	-	N	6,906.52	964.3	49.6	1,661	13.3	561.1	4,827	2,499.5	11,360	+6.0
S-01	12.8	7.5	2,050	N	6,875.76	303.1	303.1	1,388.7	1795	2,137.6	5,594	2,678.7	14,312	-14.8
S-02	13.9	8.5	4,330	N	6,878.08	160.1	212.8	149.	1.54	49.5	1,445	170.4	2,396	-21.8
S-03	12.9	7.4	3,170	N	6,886.41	179.2	179.6	273.5	0.78	88.4	1,908	1,129.9	4,882	-27.9
S-04	13.8	8.7	3,130	N	6,869.51	108.2	384.5	269.3	1.56	316.2	2,709	413.1	3,672	-14.7
S-08	11.7	9.2	2,070	0.3	6,865.82	223.3	148.6	398.7	6.61	12.1	1,373	139.8	2,244	-7.4
32-41	12.0	8.1	5,600	N	6,968.79	545.2	136.6	178.9	7.03	47.1	2,997	1,337.1	6,044	-7.4
32-42	13.8	7.4	10,000	N	6,900.73	1,484	539.0	743.5	10.92	60.41	5,850	1,534.7	11,868	-10.6
32-43	14.1	7.1	5,700	N	6,904.28	1,480.	404.0	861.2	2.71	717.2	3,563	123.7	6,468	-0.8
32-50	14.2	7.2	7,400	N	6,899.76	571.3	466.5	466.5	9.73	590.6	3,004	1,445.4	7,536	-8.8
32-51	13.7	8.6	4,380	N	6,897.33	1,00.	452.8	453.5	3.90	537.5	3,440	182.4	5,424	-13.1
32-52	13.7	7.6	2,750	N	6,893.37	688.4	323.0	341.6	1.64	256.2	2,097	98.9	3,120	-20.5
M-22	12.9	7.5	5,500	N	6,851.50	317.4	390.4	177.6	3.99	13.6	4,334	207.4	7,148	-7.6
M-23	12.3	7.2	3,170	N	6,840.41	1,402	481.6	296.1	8.15	458.0	2,485	83.9	6,064	-14.1
M-24	13.2	7.2	4,890	N	6,830.11	191.3	549.0	195.0	0.78	227.3	2,614	130.5	5,968	-15.2
Mill circuit H_2SO_4	-	-	3,200	-	-	315.1	577.2	160.3	4.49	225.6	2,005	132.1	3,920	-11.4
									2.34	300.3				+5.8

sulfate anions were separated from solution by a sulfate selective anion exchange column; Biorad AG1-X8 (Nehring and others, 1977). Sulfate was eluted from the columns with 100 mls of 0.5 M sodium chloride (NaCl) at a column flow rate of 0.43 ml/min. Elution of sulfate anions was quantitative (100% yield) to prevent isotopic fractionation.

Sulfate was precipitated from the purified eluant as $BaSO_4$. The solution was first acidified with concentrated hydrochloric acid and bubbled with nitrogen gas to remove any carbonate that precipitated with $BaSO_4$ as $BaCO_3$. Twenty-five mls of 0.25 M $BaCl_2$ solution were then added to each beaker to precipitate $BaSO_4$.

$BaSO_4$ was allowed to settle overnight in covered beakers; the precipitate was washed and filtered through a 0.45µ Millipore filter apparatus the following day. Purified $BaSO_4$ was dried on filter papers in a 110° C oven.

Purified $BaSO_4$ was quantitatively converted to sulfur dioxide in a vacuum system (Bailey and Smith, 1972). Twenty mg of the $BaSO_4$ sample were measured into a 7 mm pure quartz tube that was slipped into another 9 mm diameter quartz tube. The quartz tube was connected to a vacuum line and the entire vacuum system evacuated to approximately 10^{-3} Torr.

The sample tube was heated to 1100° to 1200° C with a double tipped oxygen-methane torch. The quartz tubes fused together and sulfur dioxide gas bubbled out of the molten mixture. Escaping SO_2 was frozen out in a liquid nitrogen cold trap protected by a dry ice ethanol water trap. The volume of the SO_2 gas was measured to determine yield; typically 95%. SO_2 gas

was then transferred into a stopcock, removed from the vacuum system, and was ready for mass spectrometric analysis.

All samples were isotopically analyzed at the University of Arizona Isotope Geochemistry Laboratory on a Micromass-602C dual collection mass spectrometer. Overall accuracy was checked on a known $BaSO_4$ standard obtained from the USGS Isotope Laboratory, Denver, Colorado; precision of 0.37‰ was obtained. The mass ratios were corrected for variable ^{18}O content of the sample gas. Many of the extreme samples were checked; their reproducibility was ± 0.5‰.

Interpretation and Analysis of Results

Following sections of this report present three hypotheses that could explain observed sulfur isotope composition of dissolved sulfates from the Kerr-McGee mill site. Each hypothesis is tested for accordance with observed hydrologic and chemical data and with mining and milling practices. The only hypothesis consistent with all data is that there are at least three significant sulfate sources in the alluvial aquifer. Mixing of these sources and pre-mining hydrologic conditions in the alluvium are discerned using sulfur isotope data.

Isotopic data presentation

Figure 15 is a frequency distribution of $\delta^{34}S$ values of samples from Kerr-McGee's section 31 mill site. Patterned areas of Figure 15 indicate the geographic location of sampling sites with respect to Arroyo del Puerto and evaporation ponds.

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Mill circuit sulfuric acid

Waters from ponds #1 and #3 and wells west of Arroyo del Puerto less than 1/4 mile from pond #3

Water from wells west of Arroyo del Puerto more than 1/2 mile south of ponds #1 and #3.

Waters from the mill reservoir, Arroyo del Puerto, and wells east of Arroyo del Puerto

Figure 15. Frequency diagram showing location and $\delta^{34}S$ of samples

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Hatched bars signify waters from ponds and wells adjacent to
ponds. Dotted bars signify waters from wells far south of the
ponds and west of Arroyo del Puerto. Solid bars indicate
waters east of Arroyo del Puerto, the mill reservoir, and
Arroyo del Puerto.

Hypothesis I: Single sulfate source

One explanation of observed δ^{34}S values is that sulfuric
acid leachate with historically variable sulfur isotope com-
position is the single significant sulfate source in the alluvial
aquifer. Although detailed records of historical sulfuric acid
use are not available, mass balance approximations indicate that
sufficient H_2SO_4 has been added in the milling process to account
for all dissolved sulfate in the alluvial aquifer.

If all sulfate in the alluvial aquifer originated from pond
leachate, the range of δ^{34}S values of sulfuric acid would have
to be 38‰ (-28‰ to +10‰). Historical variation in sulfur isotope
composition of sulfuric acid could be caused either by changes
in source of sulfur from which acid is manufactured or by vari-
able fractionation of sulfur during the manufacturing process.
Kerr-McGee manufactures sulfuric acid at the section 31 mill site.
Presently sulfur is supplied to Kerr-McGee from sour gas fields
in Oklahoma (D. Kumpf, Kerr McGee, personal communication, 1981).
Historical sulfur suppliers are unknown, but if sulfur has always
been supplied by the same source such a range of isotopic com-
position is highly unlikely.

Fractionation could occur during production of sulfuric

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acid. Production of sulfuric acid from sulfur is shown in the
following reactions:

$$S + O_2 \rightarrow SO_2 \tag{3}$$

$$SO_2 + O_2 \xrightarrow[\text{catalyst}]{V_2O_3} SO_3 \tag{4}$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \tag{5}$$

Reactions (3) and (5) are spontaneous and quantitative, hence
fractionation could not occur during these. Reaction (4) may
yield only a 60% conversion of SO_2 to SO_3, however SO_2 is
normally recycled allowing little fractionation to occur.

If all sulfate in the aquifer originated as pond acid, the
following scenario is most reasonable.

Sulfate from this earliest period of leaching now occupies
the zone greater than ½ mile south of ponds #1 and #3 west of
the river (wells 5-02 and 5-04). δ^{34}S values and the flow
directions for pond seepage indicate that earliest values of
δ^{34}S were in the range of -28‰ to -21‰. Later sulfates, with
δ^{34}S between -8‰ and -16‰ now occupy the zone east of the river,
probably mixed with mine discharge waters which fall in the same
isotopic range. The most recent sulfates are heavier, about
+5‰, and have now contaminated the alluvium around the ponds.

The single source hypothesis suffers from profound defici-
encies. Sulfates are very high in all wells sampled. A
simple calculation demonstrates that the sulfates in distal
wells cannot have come from the ponds. Well 32-5? will be
used as an example. Given the conditions of a step-function

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input of sulfate under pond #6 (the closest pond) at concentration C_o,

$$C/C_o = \frac{1}{2} \text{ erfc } \left(\frac{L - \bar{V}t}{2\sqrt{D_L t}} \right) \quad \text{(Ogata, 1970)} \quad (6)$$

where C is the concentration of sulfate at well 32-57 (assumed at the start to be zero); erfc is the complementary error function; L is the distance from well 32-57 to the pond, 4000 ft; $\bar{V}$ is average water velocity; t is time of flow; and D_L is dispersion coefficient, defined as $\bar{V} \cdot \alpha$. The dispersivity, α, is in feet. If very high estimates are made that $\bar{V} = 50$ ft/yr and $\alpha = 500$ ft, and the certain retardation by unsaturated zone flow is ignored, C/C_o reaches only 0.6% in 24 years, the time since pond #6 was constructed.

Furthermore, this hypothesis fails to explain similarity between isotopic composition of Arroyo del Puerto and mill reservoir waters, which originate from mine dewatering, and those of alluvial wells east of Arroyo del Puerto. The former should be reflective of present [34]S values in the tailings ponds and adjacent wells. The single source hypothesis can be discarded.

Hypothesis II: Two sulfate sources

A second hypothesis is that there are two significant sulfate sources in the alluvium; pond acid and sulfates originating from formation waters produced by mine dewatering. Each source has a characteristic $\delta^{34}S$; +5‰ for pond waters and -25‰ for formation waters. Waters composed of a mixture of pond and mine

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waters are expected to have intermediate $\delta^{34}S$ values; the observed $\delta^{34}S$ value of mixed samples depends on the percent contribution of the two sources.

This hypothesis requires that wells close to ponds #3-#6 contain pond acid sulfate, that waters east of Arroyo del Puerto contain a mixture of pond and formation sulfate, and that wells south and west of the ponds contain waters initially pumped from mines that are uncontaminated by pond sulfate due to flow path length and travel time.

Flow paths indicated in Figure 11 are consistent with this scenario, but several major discrepancies exist. Average compositions of each water group are:

	$\delta^{34}S$ (‰)	SO_4 (mg/1)
wells near pond (A1, B2, C3, S12)	+ 5	4818
wells east of ponds (M-22, 23, 24; 5-01, 08; 32-43, 51, 57)	-12.5	2278
"light" wells (5-02, 04; 32-52)	-26	2234

Well 32-52 far east of Arroyo del Puerto has a very light $\delta^{34}S$ of -28.5‰ which should indicate the presence of only formation water produced when mining began. Its location among wells producing water of mixed origin indicates that it should also produce "mixed" water. $\delta^{34}S$ mass balance requires that wells east of ponds contain approximately 64% mine-origin water and 36% pond water. However a sulfate balance suggests that these

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mixed-origin waters contain 98% formation-water and 2% mill-origin water. These disparate results do not support a two-source hypothesis. Furthermore, as with the single-source hypothesis, implausibly high flow rates and dispersivity are necessary to deliver formation water sulfate to distal wells. Therefore, the two-source hypothesis is abandoned.

Hypothesis III: Three sulfate sources

A third explanation of sulfate isotope composition in the study area is that at least three sulfate sources are present. Acid pond sulfates have a δ-value of approximately +5‰. Sulfates in contaminated water from the Tres Hermanos have a δ value of about -28‰. Mineral sulfates or sulfates in in waters from a pre-mining water table in alluvium east of Arroyo del Puerto and sulfates in formation waters produced by mine dewatering have $\delta^{34}S$ of -13‰ and -11‰, respectively. (The last sulfate sources are grouped because changes in isotopic composition due to mixing of these waters would be difficult to detect.) The three sources and their sulfur isotope and sulfate compositions are shown below.

	$\delta^{34}S$ (‰)	SO_4 (mg/l)
pond sulfates (A1, B2, C3, S12, P-1)	+5 (average)	3000 to 8000
Tres Hermanos-b (32-52, 5-04)	-27.9 to -28.5	1908 to 2087
mine discharge and pre-mining water table or mineral sulfates (IX; 32-57; M-22, 23, 24)	-11.0 to -13	1188 to 4000

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A three-source hypothesis is supported by the following sulfur isotope data. The tailings ponds and associated wells show a mean $\delta^{34}S$ of +5‰. Mill reservoir waters (IX discharge) presently contain sulfate with $\delta^{34}S$ of -11 ‰. At sampling point P-12 downstream, Arroyo del Puerto water has $\delta^{34}S$ of -8.4‰ indicating either input of heavier acid sulfate from ponds or input of heavier sulfates by the mine upriver. As described in the preceding section, southeastern alluvial wells appear to contain uncontaminated water typical of mine discharge. However, east of Arroyo del Puerto, sulfate concentration generally increases downgradient from ponds as exhibited by wells 32-41, 32-43, and 32-47. This phenomenon contradicts the hypothesis that increased sulfate concentration is due to mill pond seepage; and requires the presence of a third sulfate source, either a pre-mining water table in isolated areas of alluvium with exceptionally high sulfate concentration (near 4000 mg/l), or dissolution of mineral sulfate. Wells 32-52 and 5-04 have very low (~28‰) $\delta^{34}S$ values which cannot be accounted for by mixing of any of the other three heavier sources. Well 5-04 is completed in Tres Hermanos-b; well 32-52 is reported to be completed in alluvium (Ganus, 1980), however, well depth is 88 ft., thickness of alluvium is approximately 90 ft. (Figure 8) at that site and due to difficulty in distinguishing alluvium from Tres Hermanos, the well could easily be completed in Tres Hermanos. Tres Hermanos waters near the mill site are reported to be highly concentrated (2000 to 2700 mg/l) in sulfate (Brod, 1980).

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To test the three-source hypothesis the concept of mixing curves is introduced.

Theory of mixing curves

If three different groundwaters contain concentrations C_1, C_2, and C_3 of a conservative tracer solute and δ_1, δ_2, and δ_3, isotope ratios of the solute, the solute concentration, C_m, of a mixture of these waters is, by mass balance

$$C_m = C_1 X_1 + C_2 X_2 + C_3 X_3 \tag{7}$$

where X is the fraction of groundwater in the mixture and

$$X_1 + X_2 + X_3 = 1 \tag{8}$$

Similarly, the isotope ratio of the mixture is

$$\delta = (C_1 \delta_1 X_1 + C_2 \delta_2 X_2 + C_3 \delta_3 X_3) / C_m \tag{9}$$

Concentrations and isotope ratios of the sulfates at the Ambrosia Lake site are known. Therefore, in principle, the three equations and three unknowns (fractions of groundwater in the mixture) from even a three source system are completely defined. $\delta^{34}S$ plotted against sulfate concentration would represent end members (unmixed sources) as discrete groups. Mixtures of any two end members would plot along a straight line connecting those two groups. Three-source mixtures would plot in the area defined by the three "mixing lines".

However, little contrast is shown in sulfate concentrations throughout the system, indicating, if the three-source hypothesis were correct, that all sources have very high sulfates.

In such a case, equation (7) reduces to equation (8) and the mixing line method would not work. Therefore, to test hypothesis III, an additional conservative tracer associated with one of the sources must be identified. The obvious choice at the Kerr-McGee site is chloride, which is added in copious amounts in the ion exchange stripping and solvent extraction step of the uranium milling process.

Chloride is recognized as a good groundwater tracer; it is refractory and normally does not demonstrate sorption. At low pH, where anion exchange can be important, chloride is weakly sorbed, and should be more mobile than even sulfate. Chloride concentration in present ion exchange solution entering the solvent extraction circuit is 45,000 mg/l (Wm. Ganus, Kerr-McGee, personal communication, 1981). Liquid effluent discharged to pond #1 showed chloride concentrations of 1500 to 3000 mg/l and wells adjacent to the pond showed chloride concentrations from 3000 to 4000 mg/l. Average chloride pumped from the mines is near 50 mg/l although there is about 100 mg/l variance (Wm. Ganus, Kerr-McGee, personal communication, 1981). Most of the wells far from the tailings ponds have chloride values near 100 mg/l.

Figure 16 is a plot of chloride versus $\delta^{34}S$ for samples from the study area. The end member for natural sulfates from previously isolated areas of the alluvium-Tres Hermanos is represented by wells 5-04 and 32-52 (point A). These sources of water exist where the alluvium is in hydraulic connection with the Tres Hermanos layers and are apparently isolated from
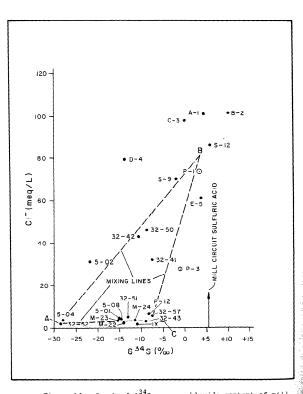
Figure 16. Graph of $\delta^{34}S$ versus chloride content of mill site samples

the other alluvial waters. These waters are separated from other possible sources on basis of their extremely low $\delta^{34}S$ values of -27‰ and -28‰. Chloride is low as expected and shows no influence of pond seepage; sulfates are naturally high, about 2,500 mg/l.

A second source component of sulfates that originates from mill pond seepage appears in wells close to ponds #1 and #3 on the west side of the Arroyo del Puerto. End members sampled were A-1, S-12, P-1, E-5, C-3, and B-2, but the end point is less defined than the Tres Hermanos end point. These samples scatter around an average $\delta^{34}S$ value of +5‰ and show chloride concentrations greater than 2000 mg/l. Chloride concentrations also show considerable scatter; 80 meq/l or 2840 mg/l chloride was chosen as the end member concentration (point B). Sulfate concentrations are higher than natural waters, as expected, and vary from 3000 to 8000 mg/l. Pond #1, the ultimate source of the acid sulfate, shows a sulfate concentration of 37,483 mg/l.

Scatter in $\delta^{34}S$ values of acid sulfate might be due to use of different sulfur sources to produce sulfuric acid. Fractionation by bacterially-assisted anaerobic reduction or by ion exchange produces heavier residual sulfate. Only B-2 ($\delta^{34}S = +10.5$) shows significantly heavier sulfate than pond acid suggesting that fractionation processes are not important.

Chloride concentrations in wells S-12, C-3, A-1, and B-2 are greater than that in pond #1. This can be explained by milling practices that have introduced amounts of chloride that varied temporally. Concern has been voiced about amounts of

chloride previously used in milling and about change in mill use of chloride (Wm. Ganus, Kerr-McGee, personal communication, 1981). Therefore a recent decrease in mill chloride use is not unlikely. A second possibility is that a density gradient exists in pond #1. Pond #1 contains 44,484 mg/l total dissolved solids, hence sufficient dissolved solids exist to maintain a considerable density gradient. If so, the sample, taken from the top of pond #1, might not represent more concentrated waters near the bottom infiltrating underlying alluvium.

Mine dewatering discharge and natural alluvial water or dissolved sulfate minerals constitute a third sulfate source. (As previously noted, these waters are isotopically indistinguishable, hence they are grouped.) The end member chosen for $\delta^{34}S$ (point C, Figure 16) is well 32-57. It is most upgradient in a pre-mining water table and furthest from ponds. Therefore, it is least likely to have been affected by Tres Hermanos or pond waters. Chloride concentration selected is 125 mg/l; $\delta^{34}S$ is -7.6‰. Mine discharge waters would fall on A-C mixing line (Figure 16) and would therefore be indistinguishable from a mixture of natural alluvium and Tres Hermanos waters.

Points scattered between these end member groups A, B, and C (Figure 16) are mixtures of two or three of the source component waters. These samples include 5-02, 32-42, 32-50, 32-41, S-9, E-5, and pond #3.

Pond #3 is a known mixing point. It receives decant from pond #1 and seepage into the old Arroyo del Puerto channel pumped from behind the dam. Its location on the mixing curve shows influence from both pond and alluvial water end members. Its $\delta^{34}S$ value is -1.1‰. An isotopic mixing ratio indicates approximately two-thirds of the water in pond #3 is of ground-water origin and one-third decant from pond #1.

Wells 32-41, 32-42, and 32-50 all lie within the mixing triangle shown in Figure 16; showing probable contribution from all waters including mine discharge. Sample 32-41 is a mixture of pond, alluvial, and Tres Hermanos waters, whereas 32-42 and 32-50 are predominantly Tres Hermanos and pond water (approximately 50% of each). A mixture of Tres Hermanos and alluvial water is consistent with hydrologic data. As previously noted, at least one well completed in Tres Hermanos exhibited artesian flow; alluvium rests upon Mancos Shale or Tres Hermanos throughout the basin. The influence of Tres Hermanos waters increases to the east and south. This would be expected if Tres Hermanos waters were seeping upward into the alluvium as pre-mining alluvial water flowed toward the south.

Well 5-02 falls slightly outside the mixing curve between the pond and Tres Hermanos sulfate groups. Its isotopic composition is about -22‰. Its chloride concentration suggests some influence of pond seepage; chloride is 1000 mg/l higher than either 5-02 or 32-52. Based on isotopic mixing proportions a $\delta^{34}S$ value of -22‰ indicates about 20% sulfate comes from the ponds and 80% from the natural background source. Chloride balance, on the other hand, indicates that nearly 40% of the water is of pond origin. This difference may be due to variable chloride input, discussed previously, or to more effective

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retardation of sulfate than of chloride from the pond. Sulfate, more strongly adsorbed than chloride in anion exchange process, would be expected to be more effectively retarded. Well S-9 is geographically on a line between the ponds 5-02 and 5-04, a Tres Hermanos end member well. Its position suggests that it should be a mixture of Tres Hermanos waters and pond waters, with pond waters predominating. The A-B mixing line is in excellent agreement; both chloride and δ^{34}S balances indicate about 80% pond water and 20% Tres Hermanos water.

Well D-4 lies well outside the mixing trangle. Its δ^{34}S is considerably lower (-13‰) than other wells adjacent to pond #3 and its sulfate concentration is only 867 mg/l, the lowest value observed. In contrast to its low sulfate, the chloride concentration in D-4 is 2837 mg/l. Well D-4 has always shown a different chemistry from other wells adjacent to pond #3. This well is believed to be completed in the Mancos Shale that underlies a large area beneath pond #1 (Wm. Ganus, Kerr- McGee, personal communications, 1981). If chloride concentration is an accurate indication of pond seepage, the Mancos must have some highly effective mechanism for sulfate removal either by adsorption or precipitation. Ion exchange effects, which can be significant in clayey materials, are indicated by the water chemistry shown in Figure 17. On graph D, sodium, which in pond seepage should have equivalent concentration with chloride, falls far below the sodium-chloride equivalence line (dashed line in Figure 17-D), while calcium (graph F) shows the highest concentration of all samples. This strongly suggests that sodium cations in pond
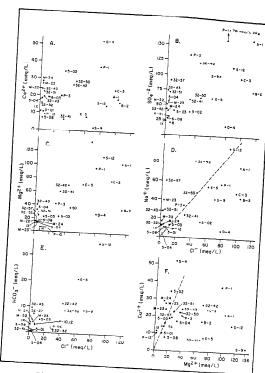
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Figure 17. Comparison of water chemistry analyses in the vicinity of the Kerr-McGee Ambrosia Lake uranium mill. Graphs A-E are meq/l solute versus meq/l chloride. F is a comparison of magnesium and calcium. (dashed lines indicate equivalence)

seepage waters have replaced calcium cations in clay minerals, depressing sodium and raising calcium concentration above levels for pond waters.

At the low pH of 5.5 in D-4, anion exchange should also be important. Low sulfate concentration suggests that waters depleted of sulfate by anion exchange are infiltrating the aquifer. If this is the case, retarded sulfates will reach D-4 at some future time. Sulfate levels will then increase. Continued monitoring of D-4 sulfates may provide information about sulfate transport in the Mancos Shale.

The remaining groundwaters sampled are M-22, M-23, and M-24 which monitor lined evaporation ponds to the southeast of the tailings ponds; 5-08 and 5-01 south and east in the alluvium; and 32-43 and 32-51 to the east. All fall on the A-B mixing line, grouped geographically from south to north. Southern wells show approximately 40% Tres Hermanos waters; northern wells show approximately 10% Tres Hermanos waters. Exceptions are M-24, about 25% and 32-51 about 30% Tres Hermanos water. As stated before, the influence of mine water would not be observable; sulfate balances imply that this influence is negligible. No wells along the A-B line show tailings pond contamination. P-12, a river sample taken down river from the tailings ponds may have 5% tailings water. If true, this is higher than Ganus's (1980) estimate of approximately 1%, but scatter in the data could also be responsible for the water's chloride and $\delta^{34}S$. Well 32-52 has anomalously light sulfate for an alluvial

well. Its chemistry is very similar to that in 5-04. This is considered to be persuasive evidence that this water is isolated from the other alluvial waters and representative of Tres Hermanos waters; hydrologic evidence for this conclusion was presented previously. Tres Hermanos flow into the alluvium at this point is strongly implied.

One issue, not yet fully clarified, is the origin of the pre-mining alluvial water sulfate or mineral sulfate source. Hydrologic data support the existence of a pre-mining water table in the alluvium. The thickness of alluvium far east of Arroyo del Puerto can be determined from measured water levels and isopach contours (Figure 8). If alluvium were dry prior to mining, maximum gradient for the first seepage from ponds or Arroyo del Puerto is that from the surface water to the base of the alluvium (see Figure 8). Flow necessary to saturate a dry, pre-mining aquifer within the 24 year period of mining at the site can be calculated from this maximum gradient and hydraulic conductivity and porosity of alluvium reported by Ganus (1980). For example, a gradient of 77 feet/4000 feet is the maximum possible from the eastern edge of pond #6 to well 32-57. With an average hydraulic conductivity of 10 $gal/ft^2/day$, porosity of 0.2, and aquifer thickness of 70 feet, flow per cross sectional foot is 13.5 gal/day and 73 years is required to fill this volume of aquifer to its present level. Unsaturated flow, lower historical gradient, and volume of aquifer east of well 32-57 have been ignored in this estimate, yet incorporation of each would substantially increase the time. Thus, based on

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available hydrologic data, the alluvium had a pre-mining water table aquifer; this water was very poor quality. Both increasing sulfate concentration with distance east of ponds and low chloride levels in distal wells also support existence of premining alluvial water. Sulfate concentration could be due to oxidation of sulfide minerals or dissolution of sulfate minerals coupled with oxidation of sulfide minerals. Either mechanism could produce observed $\delta^{34}S$ values of -8‰, which are much lighter than normal groundwater sulfate. If, in contradiction to our hydrologic calculation, the alluvium were dry prior to mining, observed chemical data could be explained by dissolution of sulfate minerals by infiltrating Arroyo del Puerto seepage.

Conclusions

This study used isotopic signatures of sulfates to show a plausible mixing pattern for three sulfate sources in a complex alluvial system. Mixing curve theory, based on one, two, and three sources of sulfate, was used to test hypotheses based on sulfur isotope data. Hypotheses were also tested for consistency with hydrologic and chemical data. The study demonstrated that sulfur isotopes can be applied in conjunction with chemistry and hydrology to trace contaminated waters and produce reasonable estimates of mixing patterns in complicated aquifer systems. This study also verified that substantial variations in $\delta^{34}S$ values may exist between industrial and natural-origin sulfates in a groundwater system, thus providing impetus for further similar studies concerning groundwater contamination.

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Our study indicates that the natural alluvial waters at this site may be more extensive than previously thought, but that they are of very poor quality, more than 2500 mg/l sulfate. The origin of these sulfates is probably weathering of sulfide minerals or dissolution of mineral sulfates produced at least partly by such weathering.

Results of this study were based on principles of mixing theory. Measurement of the stable isotope ratios, $^{34}S/^{32}S$, provided a third source-specific variable that was used in conjunction with other chemical data to develop a three-source mixing scene. This resulted in the ability to distinguish a possible third source component that could not be distinguished based on chemical and hydrological information alone.

Problems in applying mixing theory in this study included the scatter in δ-values and concentrations of the designated end member sources. Two variables, each with a substantial uncertainty range, had to be used to generate mixing curves. End member samples were insufficient to unequivocally designate natural alluvium sulfate source components. Possible retardation of sulfates by anion exchange introduced further uncertainty. Finally, insufficient information is available on past operations or pre-mining hydrology to deal properly with transient conditions in this alluvial system. Despite these difficulties data are sufficiently consistent with interpretation to generate confidence in our conclusions.

Several additional benefits were gained in this tracing

study. Support of the Pueblo of Laguna and assistance of several entities, the Bureau of Indian Affairs, Environmental Improvement Division of New Mexico, and Kerr-McGee Nuclear Corporation allowed testing of this new tool, stable isotopes of sulfur, for assessment of contamination. New techniques are seldom applied to study industrial contaminants at a private industrial site. The study has generated additional data on ^{34}S isotopic ratios for both anthropogenic and natural freshwater sulfate sources. It has also provided an additional data type at each location so that comparisons can be made with existing chemical and hydrologic data to gain further insights. Of particular interest is migration of more toxic substances.

This isotopic study has also generated questions about possible applications of ^{34}S isotopes to other areas. ^{34}S isotopes from dissolved sulfates and sulfide minerals may develop a better understanding of weathering rates of sulfide minerals, and thus the oxidation of mined ore bodies that provides continuing release of soluble heavy metals and radionuclides. Feenstra and others (1981) emphasized the importance of understanding sulfide oxidation processes in uranium tailings piles, particularly if remedial action is planned. Such understanding would be important in other mine tailings types, such as those from coal, iron, and copper operations. Precipitation, adsorption, and neutralization processes associated with seeping industrial ponds and tailings might also be studied using stable sulfur isotopes in conjunction with other species of interest.

We suggest that monitoring of sulfur isotopes be continued at the Kerr-McGee Ambrosia Lake site. Vertical movement of tailings pond waters was not investigated in this study, but information from mine seeps and Dakota wells could easily be integrated into our work. Variation of ^{34}S and chloride at several wells, in particular D-4, 5-02, and S-9, may enable estimates of velocities of more toxic species in this system by determining extent of adsorptive retardation.

Plans for future study

We are now developing analytical methods for determination of oxygen isotope ratios of sulfate. New data being produced by EID on hydrogen and oxygen isotopes in water. These will be incorporated into this study and will provide a rigorous test on reported conclusions.

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